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THE CRYSTAL STRUCTURE OF DIPOTASSIUM TETRANITROETHIDE

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ABSTRACT

The structure of dipotassium tetranitroethide $K(NO_2)_2CC(NO_2)_2K$ has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the centro-symmetric space group $C2/c$ with cell constants of $a = 13.03$ A, $b = 7.56$ A, $c = 13.55$ A, and $\beta = 140.87^\circ$. Each unit cell contains four molecules, with the anions centered on two-fold rotation axes. Atomic and thermal vibration parameters were refined by isotropic least squares method to give a final structure with an R value of 12.3%. The configuration of each carbon atom and its three substituents is planar within experimental error. There is a twisting of the nitrogen atoms about the C-C molecular axis to produce an angle of 63.1° between the N-C-N planes in the tetranitroethide anion. The C-C bond distance is 1.43 A.

INTRODUCTION

In previous investigations, the crystal structures of the stable carbanion salts ammonium tricyanomethide², pyridinium dicyanomethylide³, and potassium paranitrophenyldicyanomethide⁴ were determined. It was thought that the structure determination of dipotassium tetranitroethide $K(NO_2)_2CC(NO_2)_2K$ would be an interesting extension of the previous work because this salt contains a polynitro-substituted dicarbanion.

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EXPERIMENTAL

Dipotassium tetranitroethide was prepared from the reaction of tribromonitromethane with an anhydrous ethanol solution of potassium iodide by the method of Hunter.⁵ Well formed rhombohedral single crystals of dipotassium tetranitroethide were obtained by leaving loosely covered beakers of a saturated solution prepared from the purified salt and water at room temperature in a refrigerator until the crystals formed.

Crystals with a diameter of about 0.2 mm were selected as specimens for X-ray diffraction analysis and mounted on glass fibers. Weissenberg and Rotation photographs showed the dipotassium tetranitroethide unit cell to be monoclinic with cell constants of $a = 13.02 \pm 0.02$ Å, $b = 7.56 \pm 0.02$ Å, $c = 13.55 \pm 0.02$ Å, and $\beta = 140.87 \pm 0.50^\circ$. The c rotation axis was found to be coincident with the needle axis of the crystal while the b rotation axis was perpendicular to the needle axis and coincident with the shorter edge diagonal of the needle.

All reflections with $h + k = 2n + 1$ were absent, indicating a C centered unit cell. Systematic absences were also observed for $h0l$ reflections with $l = 2n + 1$ which showed the presence of a c glide-plane perpendicular to the b axis.

The centro-symmetric space group $C2/c-C_{2h}^6$ and the noncentro-symmetric space group $Cc-C_s^4$ are the only monoclinic space groups containing symmetry elements consistent with the above absences. These space groups can not be distinguished from each other on the basis of systematic absences. However, our refinement of a trial structure derived by the assumption of centrosymmetric symmetry indicates that $C2/c$ is the correct space group for dipotassium tetranitroethide.

An experimental density determination by the flotation method using a mixture of CH_2Br_2 and CCl_4 gave a value of 2.24 g/cc. Comparison of this

value with the theoretical density of 0.58 g/cc for each molecule of compound contained in the unit cell showed the multiplicity to be four.

Integrated intensities for 530 independent reflections were recorded on multiple films using a Nonius integrating Weissenberg camera and nickel filtered CuK_{α} radiation. Weissenberg data were obtained around the b rotation axis for $k = 0$ through 4 and around the c rotation axis for $l = 0$ through 6. The integrated intensity values were measured with a Welch Densichron densitometer. Corrections were applied for the Lorentz, polarization, and Tunnell effects. No corrections were made for absorption and extinction.

Our initial assumption of C2/c cell symmetry with eightfold general positions and the observed multiplicity of four implied that the center of each tetranitroethide anion was on a twofold axis or a center of symmetry in a unit cell containing one potassium ion at each of eight general positions. Synthesis of the [010] Patterson projection yielded a heavy peak at $u = 0.75$ and $w = 0.60$ from which the x and z trial parameters of the potassium ion were obtained. The [010] superposition projection was calculated via the α_{gen} synthesis⁶ using these trial parameters and the relative intensities of the observed $h0l$ reflections. An image of a tetranitroethide anion centered on a twofold axis was located in the superposition projection. The positions of the peaks in this image were used to calculate the x and z anion parameters for a two-dimensional trial structure. A least-squares refinement of these parameters reduced the R from an initial value of 39% to a final value of 16%.

Heavy atom peaks in the three-dimensional Patterson synthesis showed the y parameter of the potassium ion to be ± 0.092 or ± 0.408 with the choice of sign serving to determine the direction of the positive b axis in the coordinate system. The Patterson function's inherent twofold ambiguity in the numerical value of the heavy atom y parameter was resolved by

testing the related trial structures for agreement with the experimental data. The anion y parameters for the three-dimensional trial structure were obtained from packing considerations and the knowledge that the anion must possess a twofold rotation axis.

RESULTS

A three-dimensional isotropic least-squares refinement was used to reduce the R of the trial structure from 43% to 12.3%. The calculation was done with an IBM 7094 computer using the least-squares analysis program ORFLS written by Busing, Martin, and Levy.⁷ Unobserved reflections were omitted from the refinement. During the latter stages of the refinement the original unit weighting scheme was abandoned in favor of a modified Hughes weighting scheme. With this scheme w was set equal to $1/F^2$ for all F's larger than $4F_{\min}$. For all other F's, a w of $16 F_{\min}^2/F^4$ was used*. Table 1 gives the final atomic parameters obtained by the refinement and their estimated standard deviations.

DISCUSSION

Figure 1 shows the [010] projection of the crystal structure of dipotassium tetranitroethide. The interatomic distances and angles in the tetranitroethide dianion are shown in Table 2. In nitromethane the C-N and N-O bond lengths are 1.46 and 1.21 respectively.⁸ Thus there is a lengthening of the N-O bond and a shortening of the C-N bond in the tetranitroethide ion. These changes may be attributed to resonance interactions of the type $R_2C=N^+ \begin{smallmatrix} O^- \\ \diagup \\ O^- \end{smallmatrix}$.

Perhaps the most striking feature of the tetranitroethide anion's structure is the twist of the nitrogen atoms about the C1-C2 molecular axis to produce an angle of 63.1° between the N1-C2-N2 and N3-C1-N4

* A table of observed and calculated structure factors can be obtained by writing the authors.

planes. The O1-N1-O2 and O3-N2-O4 planes make angles of 13.0° and 6.3° with the N1-C2-N2 plane respectively.

Atom N1 is 0.017 Å above the O1-C2-O2 plane while N2 is 0.035 Å below the O3-C2-O4 plane. The carbon atom C2 is 0.040 Å below the plane of its substituents N1, N2, and C1 indicating a planar carbanion configuration within the limits of the experimental error.

The vibrations in the configurations of the two nitro groups may be due to forces in the crystal lattice since each of the nitro-group oxygens is in a different chemical environment in the lattice. Each oxygen atom has two potassium ions as its nearest intermolecular atomic neighbors with corresponding O-K distance of 2.81 and 2.87 Å for O1, 2.79 and 3.00 Å for O2, 2.68 and 2.85 Å for O3, and 2.76 and 2.84 Å for O4. The shortest O-O intermolecular distance is 3.09 Å across a center of symmetry. The shortest K-C approach is 4.00 Å. The minimum O-K distance of 2.68 Å is consistent with the values of 2.73 Å in potassium paranitrophenylidicyanomethide⁴, 2.70 Å in dipotassium nitroacetate⁹, and 2.68 Å in potassium bicarbonate¹⁰.

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TABLE 1

Final Atomic Parameters for $K_2C_2N_4O_8$

Atom	X	Y	Z	B
C2	0.5621 (14)	0.5459 (16)	0.3335 (13)	0.45 (19)
O1	0.4144 (13)	0.7313 (14)	0.3173 (12)	1.62 (19)
O2	0.6274 (14)	0.6177 (18)	0.5431 (14)	2.67 (24)
O3	0.7322 (11)	0.4054 (15)	0.3553 (11)	1.33 (17)
O4	0.8270 (12)	0.4750 (15)	0.3701 (12)	1.49 (18)
N1	0.5371 (13)	0.6359 (15)	0.4042 (13)	0.82 (19)
N2	0.7098 (13)	0.4692 (15)	0.4216 (12)	0.51 (17)
K	0.3725 (3)	0.0999 (5)	0.3012 (4)	0.96 (7)

TABLE 2

Interatomic Dimensions in $K_2C_2N_4O_8$

Distance		Angle	
C1-C2	1.43 (2) A	01-N1-02	121 (2) °
C2-N1	1.40 (2)		
C2-N2	1.38 (2)	03-N2-04	119 (2)
N1-01	1.24 (2)		
N1-02	1.23 (2)	01-N1-C2	116 (2)
N2-03	1.24 (2)		
N2-04	1.27 (2)	03-N2-C2	119 (2)
N1-N2	2.43 (2)		
N2-N4	3.06 (2)	02-N1-C2	122 (2)
N1-N3	3.06 (2)		
01-02	2.15 (2)	04-N2-C2	120 (2)
03-04	2.17 (2)		
01-06	2.87 (2)	N1-C2-N2	121 (2)
03-08	2.87 (2)		
01-03	4.49 (2)	N1-C2-C1	120 (2)
01-04	3.98 (2)		
02-03	4.04 (2)	N2-C2-C1	118 (2)
02-04	2.57 (2)		

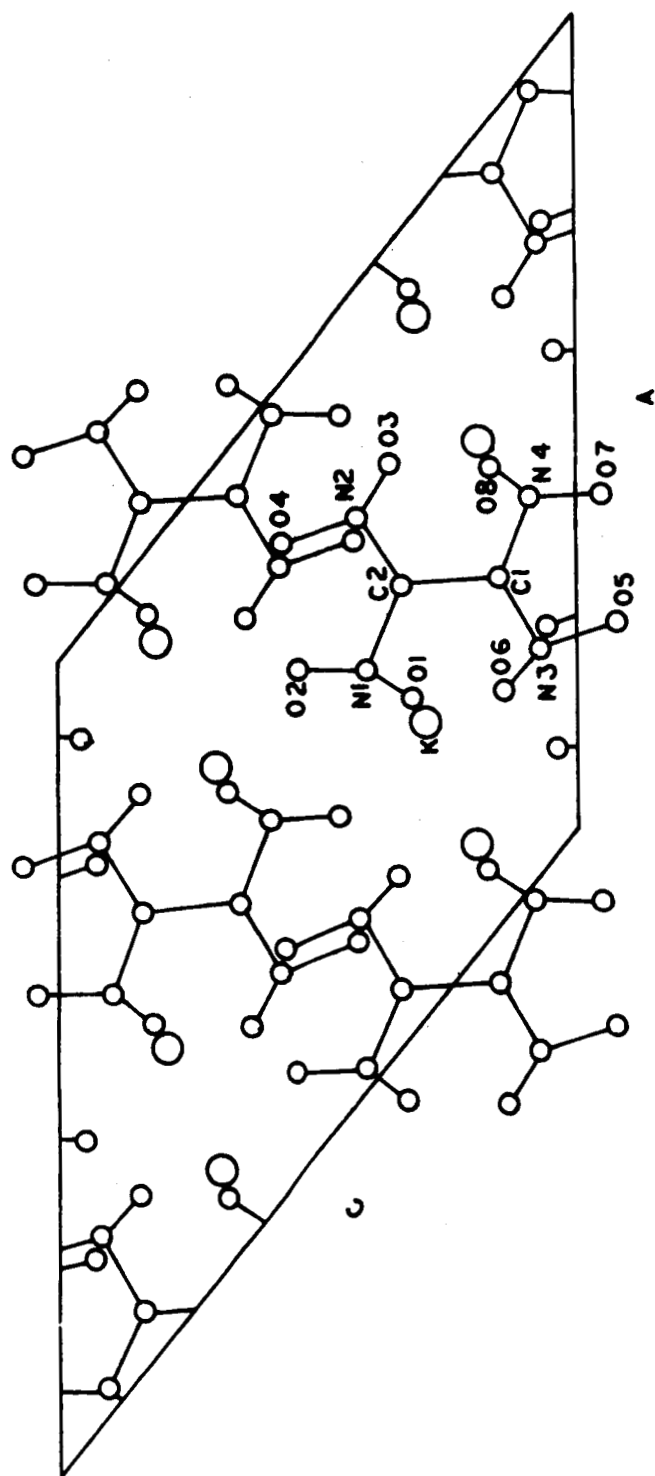


Figure 1 [010] Projection of Dipotassium Tetranitroethide